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THE DYNAMIC ELECTRIC MICROFIELD IN IONIC AND POLAR MEDIA

1989

L. Blum* and J.B. Hubbard**

* Department of Physics, University of Puerto Rico,
P.O. Box 23343, Rio Piedras, PR 00931-3343

** Thermophysics Division, Center for Chemical Engineering
National Institute of Standards and Technology,
Gaithersburg, MD 20899 - USA

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THE DYNAMIC ELECTRIC MICROFIELD IN IONIC AND POLAR MEDIA

Lesser Blum

**Department of Physics
University of Puerto Rico at Rio Piedras
Rio Piedras, Puerto Rico 00931-3343**

and

Joseph B. Hubbard

**Thermophysics Division
Center for Chemical Engineering
National Institute of Standards and Technology
Gaithersburg, MD 20899 - USA**

The dynamics of solvation is of great importance for many aspects of solution chemistry, such as spectroscopy, reaction kinetics, and dynamic light scattering. It is not surprising, then, that a number of excellent discussions exist on the subject⁽¹⁻¹¹⁾. The availability of experimental data for fast reactions in solution has prompted, very recently, theoretical research on the effects of the discrete structure of the solvent on the relaxation of internal modes in the solutes, either ionic or neutral species. In particular, we should mention the work of Wolynes⁽¹²⁾ and of Rips, Klafter and Jortner⁽¹³⁾ who discuss the relaxation of the shift of an effective hydration sphere diameter, using the mean spherical approximation (MSA) as the theory.

In the present discussion we want to study a different approach to this problem; namely, the electric microfield distribution function and its dynamic behavior.

The electric microfield distribution was first studied by Holtmark⁽¹⁵⁾, who studied the weak coupling regime. We are interested in the formulation of the microfield distribution function

$$W(\xi) = W(\xi, t) \Big|_{t=0} = \langle \delta(\xi - E_0(0)) \rangle - \int dR^v dp^v e^{-\beta H} \delta(\xi - E_0) \quad (2)$$

where we are using canonical ensemble averages of the 3-dimensional Dirac delta function $\delta(\xi)$. Our system has v particles of coordinates $R_1, R_2 \dots R_N = R^v$ and momenta $p_1 \dots p_N = p^v$. The inverse temperature $\beta = 1/k_B T$ where k_B is Boltzmann's constant and T is the absolute temperature. The Hamiltonian of the system is H . We single out a particle 0, located at the origin $R_0 = p_0 = 0$. The electrostatic field produced by a particle j , of coordinates R_j, p_j is E_{0j} .

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and

$$E_0(t) \Big|_{t=0} = E_0 - \sum_{j=1}^v E_{0j}(R_j) \quad (3)$$

Furthermore

$$E_{0j} = - \nabla \varphi_{0j}(R_j) \quad (4)$$

where $\varphi_{0j}(R_j)$ is the electrostatic potential at the origin produced by particle j . Normally the evaluation of the electric microfield would be done by expanding Eqn. (2), which entails the calculation of all v -particle distribution functions. The problem could also be reformulated in terms of a path integral, as has been done very recently¹⁶. But a more practical approach was proposed by Morita¹⁷, and more explicitly by Iglesias¹⁸. In this formalism the Fourier transform of $W(\xi)$,

$$A(\lambda) = \int d\xi e^{i\lambda \cdot \xi} \cdot W(\xi) \quad (5)$$

is introduced. It can be shown that the calculation of $A(\lambda)$ can be performed using the pair correlation functions of a modified hamiltonian $H(\lambda)$. Explicit results have been obtained in the MSA for the one component plasma on a neutralizing background¹⁹.

The static microfield problem for ionic and polar solutions was discussed recently²⁰. In the MSA, and for hard ions and spherical solvent molecules, the general result is that the microfield distribution at the center of a spherical test charge is Gaussian, of the form

$$W(\xi) = \frac{3}{2\pi m_2} \sqrt{\frac{3}{2\pi m_2}} e^{-\frac{3}{2} \frac{\xi^2}{m_2}} \quad (6)$$

where $m_2 = \langle \xi^2 \rangle$ is the mean square average of the field at the testing particle.

In several cases of interest the value of m_2 is known explicitly, such as in the MSA⁽²⁰⁾. For a mixture of ions of charge $z_i e$ ($|e|$ = electron charge), density ρ_i and hard core diameter σ_i one obtains

$$m_2 = + \frac{4\pi}{\epsilon \beta z_0} \sum \rho_i z_i g_{0i}(\sigma_{0i}) \quad (7)$$

where $g_{0i}(\sigma_{0i})$ is the pair contact distribution function, and z_0 is the charge of the test particle located at the origin. In the Onsager limit, for which the Debye screening length is zero, the following simple and exact result holds:

$$m_2 = - \frac{6}{\beta} \langle U_{\mu=1} \rangle \quad (8)$$

where $\langle U_{\mu} \rangle$ is the Onsager self energy of a dipole μ . In our case $\mu = 1$. For the primitive model electrolyte (8) reduces to (7), since the MSA second moment is exact in the Onsager limit.

The first observation is that the second moment m_2 is also the fluctuation of the electrostatic energy, $\langle \mathbf{E} \cdot \mathbf{E} \rangle$. Then the natural extension of the microfield idea to non-equilibrium situations is to study the quantity

$$L(t) = \langle \mathbf{E}(0) \cdot \mathbf{E}(t) \rangle \quad (9)$$

where $\mathbf{E}(t)$ is given by eqns. (3, 4) with coordinates $R_j(t)$ (t = time); therefore, $L(t)$ is the fluctuation (and, by the Nyquist theorem also the dissipation function) of the solvation energy. Introducing the quantity

$$W(\xi_1, \xi_2, t) = \langle \delta(\xi_1 - \mathbf{E}_0(0)) \delta(\xi_2 - \mathbf{E}_0(t)) \rangle \quad (10)$$

we see that, after a short calculation

$$L(t) = \int_{-\infty}^{\infty} d\xi_1 \int_{-\infty}^{\infty} d\xi_2 W(\xi_1, \xi_2, t) \xi_1 \xi_2 = \langle \mathbf{E}(0) \cdot \mathbf{E}(t) \rangle \quad (11)$$

we imagine now a situation in which our test particle has undergone some change, in which its charge, or better, its charge distribution has changed. Assuming that the change is permanent the system will initially be in a state in which the microfield distribution is $W_0(\xi)$. At the end of the process the microfield distribution will be $W_\infty(\xi)$. The implication is that

$$W(\xi_1, \xi_2, t) \Big|_{t=0} = W_0(\xi_1, \phi) \delta(\xi_1 - \xi_2) \quad (12)$$

and

$$W(\xi_1, \xi_2, t) \Big|_{t=\infty} = W_0(\xi_1, \phi) W_\infty(\xi_2) \quad (13)$$

Furthermore, $W(\xi_1, \xi_2, t)$ must also obey the normalization

$$\int_{-\infty}^{\infty} d\xi_2 W(\xi_1, \xi_2, t) = W(\xi_1) \quad (14)$$

at any time (t). These conditions imply that the conditional microfield probability distribution is given by

$$K(\xi, t | \xi_0) = \frac{W(\xi_0, \xi, t)}{W(\xi, 0)} \quad (15)$$

and $K(\xi, t | \xi_0)$ relaxes from a $\delta(\xi - \xi_0)$ function to the Gaussian distribution

$$K(\xi, \infty | \xi_0) = \left(\frac{3}{2\pi m_2} \right)^{3/2} e^{-\frac{3\xi^2}{2m_2}} \quad (16)$$

The time dependence of $K(\xi, t | \xi_0)$ is complicated because of the complexity of the system. It is therefore reasonable to assume that it is given by some Gaussian random process (this does not mean that ξ is a Gaussian random variable) which is characterized by a propagator and a source term. It can be verified that the boundary conditions (12-16) are satisfied if

$$K(\xi, t | \xi_0) = \int_0^t dt_1 G(t_1) \Gamma(t - t_1) \quad (17)$$

$$G(t_1) = \frac{1}{(4\pi D t_1)^{3/2}} \cdot \frac{(\Delta\xi)^2}{4Dt_1} \quad , \quad \Delta\xi = \xi - \xi_0 \quad (18)$$

$$\Gamma(t - t_1) = \frac{\Delta\xi}{\sqrt{8\pi D}} \left(\frac{3}{8\pi^2 m_2 D} \right)^{3/2} \cos \left[\xi \Delta\xi \left(\sqrt{\frac{3}{2Dm_2 t}} - \sqrt{\frac{3}{2Dm_2 t_1}} \right) \right] \quad (19)$$

The time dependence enters through the diffusion constant D , which characterizes the random relaxation process.

An alternative approach is to utilize the Fourier series representation of a Gaussian random process²² (ξ is the zero-mean Gaussian random variable) to derive a convenient and provocative form for the joint probability distribution $P(\xi, t | \xi_0)$:

$$P(\xi, t | \xi_0) = K(\xi, t | \xi_0) \exp \left[\frac{-3\xi_0^2}{2m_2} \right] \quad (20)$$

where the transition probability K , or equivalently, the conditional probability density $K(\xi_0 \text{ fixed})$, is given by

$$K(\xi, t | \xi_0) = \left[\frac{3}{2\pi m_2 (1 - M^2(t))} \right]^{3/2} \exp - \left[\frac{3}{2m_2} \left(\frac{\xi^2 + \xi_0^2 M^2(t) - 2\xi_0 \cdot \xi M(t)}{1 - M^2(t)} \right) \right] \quad (21)$$

Here $M(t)$ is the normalized microfield autocorrelation function

$$M(t) = \frac{\langle \xi(t) \cdot \xi(0) \rangle}{\langle \xi(0) \cdot \xi(0) \rangle} \quad (22)$$

where $\langle \cdot \rangle$ denotes an equilibrium ensemble average. Note that Eqn. (21) is a dynamic contact transformation in which the operator K acts on the Maxwellian distribution to produce $P(\xi, t | \xi_0)$. Berne, Pechukas, and Harp have shown that this result can also be obtained from an information theoretic approach²³.

Therefore, if ξ is a Gaussian random variable,

$$P(\xi, t | \xi_0) = \left[\frac{3}{2\pi m_2 (1 - M^2(t))} \right]^{3/2} \times \exp \left[\frac{3}{2m_2} \left(\frac{\xi^2 + \xi_0^2 - 2 \xi \cdot \xi_0 M(t)}{1 - M^2(t)} \right) \right] \quad (22)$$

Furthermore, if $M(t)$ decays as a simple exponential

$$M(t) = \exp(-\alpha t) \quad (\alpha > 0) \quad (23)$$

then we recover an Ornstein-Uhlenbeck (OU) process, which is "essentially" (allow for linear transformations of ξ and t) the only process which is stationary, Gaussian, and Markovian²⁴. It follows that, if in a microfield model such as the ion-dipole MSA, one generates an $M(t)$ which decays as a sum of simple exponentials, or if in more elaborate models one encounters sums of oscillatory exponentials, then, given that the ξ -fluctuations are time-stationary, they cannot be both Gaussian and Markovian, and in these cases it is the former condition which does not hold.

More exotic forms for $M(t)$ such, as the algebraic decay

$$M(t) = \frac{\text{const.}}{t^\alpha}, \quad t \text{ large,} \quad (\alpha > 1) \quad (24)$$

or stretched exponential

$$M(t) = \exp(-t^\beta), \quad t \text{ large,} \quad (0 < \beta < 1) \quad (25)$$

are not anticipated for electric field fluctuations in simple, non-glassy media. Algebraic decay implies that the Markov assumption has broken down, while stretched exponential behavior indicates the (more serious) apparent violation of time stationarity.

As a simple example of non-Gaussian ξ fluctuations, one might consider a so-called "dichotomic" Markov process (DMP) in which the microfield ξ takes on the values $\pm \xi_0$ with equal probability. In this case

$$K(\xi, t | \xi_0) = \frac{1}{2} \left[1 + \exp(-at) \right] \delta_{\xi, +\xi_0} + \frac{1}{2} \left[1 - \exp(-at) \right] \delta_{\xi, -\xi_0} \quad (26)$$

where a is twice the transition frequency between states and δ is the Kronecker delta function. Just as for an OU process, the autocorrelation function of a DMP is given by

$$M(t) = \exp(-at) \quad (27)$$

Therefore, if only two point correlation functions are considered, very little can be said about the stochastic process which generates microfield fluctuations, and it is for this reason that we have emphasized the importance of $P(\xi, t | \xi_0)$ and the conditional probability density $K(\xi, t | \xi_0)$.

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